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Applicant's File Ref. AD6786PCT  
Attention: D. Marsitzky

Reference D1



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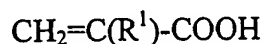
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Attention: D. Marsitzky

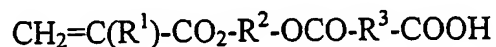
(54) Title of the Invention: RARE EARTH ELEMENT-CONTAINING RESIN AND  
METHOD OF PRODUCTION THEREOF

(57) Summary

Constitution: A rare earth element-containing resin having an excellent selective absorptivity of ionizing radiation and electromagnetic radiation, which resin comprises (a) monomer units composed primarily of methacrylic acid ester; and (b) monomer units of at least one type selected from among salts of a rare earth element selected from among lanthanum, cerium, praseodymium, dysprosium, thulium, ytterbium and ruthenium and an unsaturated fatty acid selected from among unsaturated fatty acids of the general formula



(wherein  $\text{R}^1$  is hydrogen or a  $\text{C}_{1-3}$  hydrocarbon residue) and unsaturated fatty acids of the general formula



(wherein  $\text{R}^1$  is hydrogen or a  $\text{C}_{1-3}$  hydrocarbon residue,  $\text{R}^2$  is a  $\text{C}_{2-6}$  alkylene, and  $\text{R}^3$  is a  $\text{C}_{2-6}$  saturated or unsaturated hydrocarbon residue).

Advantages: The rare earth element-containing resins of the invention have various properties, including selective absorptivity and emissivity of ionizing radiation and electromagnetic radiation originating from rare-earth elements, in addition to which they have weather resistance and increase the refractive index of the base resin.

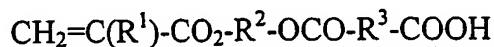
SPECIFICATION

Claims

- (1) A rare earth element-containing resin having an excellent selective absorptivity of ionizing radiation and electromagnetic radiation, which resin comprises:
- (a) monomer units composed primarily of methacrylic acid ester; and
  - (b) monomer units of at least one type selected from the group consisting of salts of a rare-earth element selected from the group consisting of lanthanum, cerium, praseodymium, dysprosium, thulium, ytterbium and ruthenium and an unsaturated fatty acid selected from the group consisting of unsaturated fatty acids of the general formula

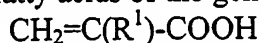


(wherein  $\text{R}^1$  is hydrogen or a  $\text{C}_{1-3}$  hydrocarbon residue) and unsaturated fatty acids of the general formula

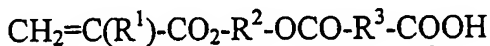


(wherein  $\text{R}^1$  is hydrogen or a  $\text{C}_{1-3}$  hydrocarbon residue,  $\text{R}^2$  is a  $\text{C}_{2-6}$  alkylene, and  $\text{R}^3$  is a  $\text{C}_{2-6}$  saturated or unsaturated hydrocarbon residue).

- (2) The rare earth element-containing resin of claim 1, wherein the amount of rare earth element, based on the resin weight, is 0.001 to 35 wt %.
- (3) A method of producing rare earth element-containing resins having an excellent selective absorptivity of ionizing radiation and electromagnetic radiation, which method is characterized by polymerizing, in an ingot mold, a mixture comprising:
- (a) a resin-forming feedstock selected from the group consisting of monomer units composed primarily of methacrylic acid ester and partial polymers thereof;
  - (b) at least one type selected from the group consisting of salts of a rare-earth element selected from the group consisting of lanthanum, cerium, praseodymium, dysprosium, thulium, ytterbium and ruthenium and an unsaturated fatty acid selected from the group consisting of unsaturated fatty acids of the general formula



(wherein  $\text{R}^1$  is hydrogen or a  $\text{C}_{1-3}$  hydrocarbon residue) and unsaturated fatty acids of the general formula

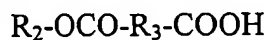


(wherein  $\text{R}^1$  is hydrogen or a  $\text{C}_{1-3}$  hydrocarbon residue,  $\text{R}^2$  is a  $\text{C}_{2-6}$  alkylene, and  $\text{R}^3$  is a  $\text{C}_{2-6}$  saturated or unsaturated hydrocarbon residue);

- (c) at least one solvent which exhibits solvency with respect to above components (a) and (b) and is selected from the group consisting of compounds of the general formula



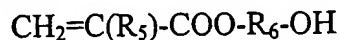
(wherein  $\text{R}_1$  is a  $\text{C}_{1-20}$  saturated or unsaturated hydrocarbon residue, compounds of the general formula



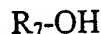
(wherein  $\text{R}_2$  is hydrogen or a  $\text{C}_{1-9}$  hydrocarbon residue, and  $\text{R}_3$  is a  $\text{C}_{1-4}$  saturated or unsaturated hydrocarbon residue), compounds of the general formula



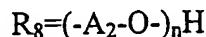
(wherein  $\text{R}_4$  is hydrogen or methyl,  $\text{A}_1$  is a  $\text{C}_{2-6}$  alkylene group, and  $n$  is 0 or an integer from 1 to 10),  
compounds of the general formula



(wherein  $\text{R}_5$  is hydrogen or methyl, and  $\text{R}_6$  is a  $\text{C}_{2-6}$  alkylene group),  
compounds of the general formula



(wherein  $\text{R}_7$  is a  $\text{C}_{3-10}$  saturated or unsaturated hydrocarbon residue, and  
compounds of the general formula



(wherein  $\text{R}_8$  is a  $\text{C}_{1-10}$  saturated or unsaturated hydrocarbon residue,  $\text{A}_2$  is a  $\text{C}_{2-4}$  alkylene group, and  $m$  is an integer from 1 to 10); and  
(d) a polymerization initiator.

### Detailed Description of the Invention

[0001]

Field of Industrial Use:

The present invention relates to resins containing a rare earth element selected from the group consisting of lanthanum, cerium, praseodymium, dysprosium, thulium, ytterbium and ruthenium. More specifically, the invention relates to rare earth element-containing resins having various properties, including the selective absorptivity and emissivity of ionizing radiation and electromagnetic radiation originating from rare earth elements. The invention relates also to a method of producing such resins.

[0002]

Prior Art:

There are many known synthetic resin additives which selectively absorb light of a specific wavelength in the visible region, including oil-soluble dyes such as azo, diazo and anthraquinone dyes. While these do have the advantage that they can be used by dissolution in the resin feedstock, as is apparent from the wavelength dependence of absorption, they absorb over a broad range in wavelength. That is, because absorption is broad, when an effort is made to achieve sufficient absorption at a wavelength near 450 nm, for example, light is absorbed over a broad wavelength range of 350 nm to 500 nm, which can be a drawback for some selective absorption applications. These dyes generally have a poor weather resistance. In certain cases, absorption will often diminish or disappear altogether with only one week of exposure to sunlight or to temperatures near 180°C.

[0003]

With regard to the absorption of electromagnetic radiation having an even shorter wavelength than visible light, such as x-rays and gamma rays, it is known that synthetic resins which are transparent in the visible region can be obtained by adding a lead compound or a bismuth compound to a synthetic resin. Based on the mass absorption coefficient ( $\text{cm}^2/\text{g}$ ), which is a numerical value that indicates the photon-absorbing

Applicant's File Ref. AD6786PCT

Attention: D. Marsitzky

ability, the absorption edge energy that accompanies orbital transitions by orbital electrons in an atom differs with the type of atom. For this reason, the mass absorption coefficient changes discontinuously in the x-ray and gamma ray energy regions. That is, upon comparing the mass absorption coefficients for lead and cerium, it is apparent that from the cerium L<sub>3</sub> absorption edge (5.723 keV) to the lead L<sub>3</sub> absorption edge (13.040 keV) and from the cerium K absorption edge (40.440 keV) to the lead L<sub>3</sub>-K absorption edge (74.960 keV), cerium has a mass absorption coefficient which is several times larger than that of lead.

[0004]

The same is true also for elements from thulium, which has the atomic number 81, to palladium, which has the atomic number 46. It can thus be seen that, at least with regard to the energy range of photons, each element has a photon absorptivity greater than that of lead which is characteristic for that element.

[0005]

Problems to be Resolved by the Invention:

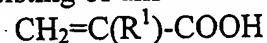
Although ordinary organic synthetic resins generally exhibit no absorption of electromagnetic radiation (infrared light, visible light, ultraviolet light, x-rays and gamma rays), the inventors have found that when rare-earth elements are included in such resins, by making use of the fact that each such element exhibits a sharp and specific absorption that is characteristic, resins can be obtained which have an unprecedented weather resistance and selective electromagnetic wave absorptivity.

[0006]

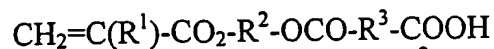
Means for Resolving the Problems:

Accordingly, the invention provides a rare earth element-containing resin having an excellent selective absorptivity of ionizing radiation and electromagnetic radiation, which resin comprises:

- (a) monomer units composed primarily of methacrylic acid ester; and
- (b) monomer units of at least one type selected from the group consisting of salts of a rare-earth element selected from the group consisting of lanthanum, cerium, praseodymium, dysprosium, thulium, ytterbium and ruthenium and an unsaturated fatty acid selected from the group consisting of unsaturated fatty acids of the general formula



(wherein R<sup>1</sup> is hydrogen or a C<sub>1-3</sub> hydrocarbon residue) and unsaturated fatty acids of the general formula



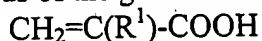
(wherein R<sup>1</sup> is hydrogen or a C<sub>1-3</sub> hydrocarbon residue, R<sup>2</sup> is a C<sub>2-6</sub> alkylene, and R<sup>3</sup> is a C<sub>2-6</sub> saturated or unsaturated hydrocarbon residue).

[0007]

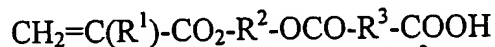
The amount of rare-earth element used in the inventive resin, based on the resin weight, is from 0.001 to 35 wt %. At less than 0.001%, the rare-earth element has little effect, whereas at more than 35%, the resin composition has poor mechanical properties.

These rare-earth elements can be incorporated in a resin by copolymerizing at least one salt selected from a group consisting of salts of the above rare-earth elements and the above-mentioned specific unsaturated fatty acids with a monomer composed primarily of a methacrylic acid ester or a partial polymer thereof. In particular, a suitable way to obtain a transparent resin that is free of [optical] scattering is a method of producing rare earth element-containing resins which involves polymerizing, in an ingot mold, a mixture comprising:

- (a) a resin-forming feedstock selected from the group consisting of monomer units composed primarily of methacrylic acid ester and partial polymers thereof;  
(b) at least one type selected from the group consisting of salts of a rare-earth element selected from the group consisting of lanthanum, cerium, praseodymium, dysprosium, thulium, ytterbium and ruthenium and an unsaturated fatty acid selected from the group consisting of unsaturated fatty acids of the general formula



(wherein  $\text{R}^1$  is hydrogen or a  $\text{C}_{1-3}$  hydrocarbon residue) and unsaturated fatty acids of the general formula

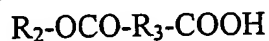


(wherein  $\text{R}^1$  is hydrogen or a  $\text{C}_{1-3}$  hydrocarbon residue,  $\text{R}^2$  is a  $\text{C}_{2-6}$  alkylene, and  $\text{R}^3$  is a  $\text{C}_{2-6}$  saturated or unsaturated hydrocarbon residue);

- (c) at least one solvent which exhibits solvency with respect to above components (a) and (b) and is selected from the group consisting of compounds of the general formula



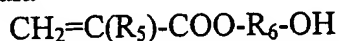
(wherein  $\text{R}_1$  is a  $\text{C}_{1-20}$  saturated or unsaturated hydrocarbon residue, compounds of the general formula



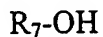
(wherein  $\text{R}_2$  is hydrogen or a  $\text{C}_{1-9}$  hydrocarbon residue, and  $\text{R}_3$  is a  $\text{C}_{1-4}$  saturated or unsaturated hydrocarbon residue), compounds of the general formula



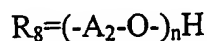
(wherein  $\text{R}_4$  is hydrogen or methyl,  $\text{A}_1$  is a  $\text{C}_{2-6}$  alkylene group, and  $n$  is 0 or an integer from 1 to 10), compounds of the general formula



(wherein  $\text{R}_5$  is hydrogen or methyl, and  $\text{R}_6$  is a  $\text{C}_{2-6}$  alkylene group), compounds of the general formula



(wherein  $\text{R}_7$  is a  $\text{C}_{3-10}$  saturated or unsaturated hydrocarbon residue, and compounds of the general formula



(wherein  $\text{R}_8$  is a  $\text{C}_{1-10}$  saturated or unsaturated hydrocarbon residue,  $\text{A}_2$  is a  $\text{C}_{2-4}$  alkylene group, and  $m$  is an integer from 1 to 10); and

- (d) a polymerization initiator.

Illustrative examples of methacrylic acid esters include alkyl methacrylates such as methyl methacrylate and ethyl methacrylate, and also cyclohexyl methacrylate, tetrahydrofuryl methacrylate, benzyl methacrylate, phenyl methacrylate, allyl methacrylate, methallyl methacrylate,  $\beta$ -naphthyl methacrylate,  $\beta$ -aminoethyl methacrylate, 2-methoxyethyl methacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, polyethylene glycol dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, pentaerythritol tetramethacrylate, trimethylolpropane trimethacrylate and halogenates of any of the foregoing methacrylates.

[0010]

The solvents represented by above general formulas (1), (2), (3), (4), (5) and (6) may be co-solvents for uniformly dissolving a rare-earth element compound in the resin-forming feedstock. Specific examples include unsaturated carboxylic acids such as methacrylic acid and acrylic acid; saturated or unsaturated fatty acids such as propionic acid, isobutyric acid, n-butyric acid, caproic acid, caprylic acid, capric acid, 2-ethylhexanoic acid, stearic acid and naphthenic acid; unsaturated alcohols such as  $\alpha$ -hydroxyethyl acrylate and  $\alpha$ -hydroxyethyl methacrylate; saturated aliphatic alcohols such as propyl alcohol and cyclohexyl alcohol; and polyhydric alcohols such as ethylene glycol, diethylene glycol and propylene glycol.

[0011]

Of these solvents, a monomer which is copolymerizable with methyl methacrylate, such as methacrylic acid, acrylic acid,  $\alpha$ -hydroxyethyl methacrylate or  $\alpha$ -hydroxyethyl acrylate, is preferred. These solvents can be used alone or as a combination of two or more thereof. The amount of solvent employed varies empirically with the type and amount of the rare earth element compound used, but is generally not more than 40 wt %, and preferably not more than 10 wt %. More than 40 wt % is undesirable because it lowers the mechanical and thermal properties of the resulting resin composition.

[0012]

The polymerization initiator used in the above copolymerization include known radical initiators such as peroxide initiators (e.g., benzoyl peroxide, lauroyl peroxide) and azobis-type initiators ( $\alpha, \alpha'$ -azobisisobutyronitrile,  $\alpha, \alpha'$ -azobis(2,4-dimethylvaleronitrile) and  $\alpha, \alpha'$ -azobis(2,4-dimethyl-4-methoxyvaleronitrile)). These polymerization initiators may be used alone or as mixtures of two or more thereof. The amount of use is 0.001 to 0.1 part per 100 parts by weight. of the resin feedstock.

[0013]

No particular limitation is imposed on the method of copolymerization used to obtain the resin of the invention, although an example of a preferred method of polymerization is cast polymerization. In the case of such cast polymerization, the mixture prepared from above components (a), (b), (c) and (d) is poured into an ingot mold comprising a cell which is made of, for example, inorganic glass, stainless steel,

Applicant's File Ref. AD6786PCT

Attention: D. Marsitzky

nickel chromium or aluminum, and a gasket, and subjected to polymerization. For special applications, radiation polymerization can be carried out at a low temperature of room temperature or less. Polymerization is generally carried out at 45 to 95°C for a period of 0.3 to 15 hours, then brought to completion at 100 to 145°C for a period of 10 minutes to 5 hours.

[0014]

In the practice of the invention, other constituents such as ultraviolet absorbers, parting agents, heat stabilizers, light absorbers for absorbing light of other wavelengths, light dispersing agents, and radiation shielding materials may also be added if necessary.

[0015]

The rare earth element-containing resin of the invention which is constituted as described above, in addition to having a selective light-absorbing ability owing to the rare earth element, also increases the refractive index of the base resin, imparts an ability to absorb x-rays, gamma rays and thermal neutron beams, and can be used as filters, lenses, transparent covers, projection screens, protective filters for ionizing radiation, scintillators and phosphors. Possible uses are not limited only to these.

[0016]

Examples are given below to further illustrate the invention, although the invention is not limited by the examples.

#### Working Example 1

Lanthanum methacrylate (8 g), n-octanoic acid (2 g), propylene glycol (1 g),  $\alpha$ -hydroxyethyl methacrylate (1 g), styrene (5 g) and methyl methacrylate (83 g) were mixed. This liquid mixture was a colorless clear liquid.

[0017]

Next, 0.04 g of  $\alpha, \alpha'$ -azobis(2,4-dimethylvaleronitrile) as the polymerization catalyst and 0.005 g of sodium dioctylsulfosuccinate as the parting agent were added and dissolved in the liquid mixture, following which the solution was degassed and poured into a conventional inorganic glass ingot mold set beforehand to a product plate thickness of 2 mm. The mold was immersed for 180 minutes in warm water at 65°C, then held for 120 minutes in an air bath at 110°C to bring polymerization to completion. The resin plate removed from the mold was clear and colorless.

#### Working Example 2

Neodymium methacrylate (4 g), lanthanum methacrylate (4 g), lauric acid (4 g) and propylene glycol (1 g) were mixed into methyl methacrylate (87 g) and dissolved, following which the solution was cast polymerized under the same polymerization conditions as in Working Example 1. The resulting resin plate was clear and pink in color.



Praseodymium methacrylate (8 g), n-octanoic acid (2 g), propylene glycol (1 g),  $\alpha$ -hydroxyethyl methacrylate (1 g), styrene (5 g) and methyl methacrylate (83 g) were mixed, following which cast polymerization was carried out under the same polymerization conditions as in Working Example 1. The resulting resin plate was clear and light yellow in color.

Working Example 4

Neodymium methacrylate (4 g), praseodymium methacrylate (4 g), lauric acid (4 g) and propylene glycol (1 g) were mixed into methyl methacrylate (87 g) and dissolved. The solution was then cast polymerized under the same polymerization conditions as in Working Example 1. The resulting resin plate was clear and light yellow in color.

Working Example 5

Praseodymium methacrylate (20 g), lauric acid (7 g), propylene glycol (4 g) and methyl methacrylate (69 g) were mixed, following which cast polymerization was carried out under the same polymerization conditions as in Working Example 1. The resulting resin plate was clear and yellow in color.

Working Example 6

Praseodymium methacrylate (20 g), lauric acid (7 g) and methyl methacrylate (73 g) were mixed, following which cast polymerization was carried out under the same polymerization conditions as in Working Example 1. The resulting resin plate was clear and yellow in color.

Working Example 7

Praseodymium methacrylate (20 g), lauric acid (7 g) and tetrahydrofuryl methacrylate (73 g) were mixed, following which cast polymerization was carried out under the same polymerization conditions as in Working Example 1. The resulting resin plate was clear and yellow in color.

Working Example 8

Thulium methacrylate (8 g), n-octanoic acid (2 g), propylene glycol (1 g),  $\alpha$ -hydroxyethyl methacrylate (1 g), styrene (5 g) and methyl methacrylate (83 g) were mixed, following which cast polymerization was carried out under the same polymerization conditions as in Working Example 1. The resulting resin plate was clear and light red in color.

Working Example 9

Neodymium methacrylate (4 g), dysprosium methacrylate (4 g), lauric acid (4 g) and propylene glycol (1 g) were mixed into methyl methacrylate (87 g) and dissolved, following which cast polymerization was carried out under the same polymerization conditions as in Working Example 1. The resulting resin plate was clear and light yellow in color.

Applicant's File Ref. AD6786PCT

Attention: D. Marsitzky

Comparative Examples

Spiron Yellow GRCH Special (a product of Hodogaya Chemical Co., Ltd.) (0.002 g) and Amaplast Yellow AGB (a product of American Aniline Products) (0.005 g) were each dissolved in methyl methacrylate (100 g), following which cast polymerization was carried out under the same polymerization conditions as in Working Example 1. Each of the resulting resin plates was clear and light yellow in color. The resin plates obtained in the working examples and the comparative examples each exhibited absorption near a wavelength of 450 nm. The spectral transmittance curves in FIG. 1 show a sharp absorption in the working examples and a broad absorption in the comparative examples. In outdoor exposure for a period of one month during summer at Otake City in Hiroshima Prefecture, the resin plates obtained in the working examples showed no change in strength, but most of the color faded in the comparative examples.

[0018]

## Advantages of the Invention:

The rare earth element-containing resin of the invention has various desirable properties, including selective absorptivity and emissivity of ionizing radiation and electromagnetic radiation originating from rare earth elements, as well as weather resistance. In addition, it increases the refractive index of the base resin. These properties enable the inventive resin to be used in filters, lenses, transparent covers, projection screens, protective filters for ionizing radiation, scintillators and phosphors.

Applicant's File Ref. AD6786PCT

Attention: D. Marsitzky

Brief Description of the Diagrams

FIG. 1 shows spectral transmittance curves for resin plates. Measurements were carried out with a Nikko spectrophotometer Model 307. Curve a shows the results for the resin plate obtained in Working Example 5, curve b is for one of the plates obtained in the comparative example (Amaplast Yellow AGB), and curve c is for another of the plates obtained in the comparative example (Spiron Yellow GRCH special).

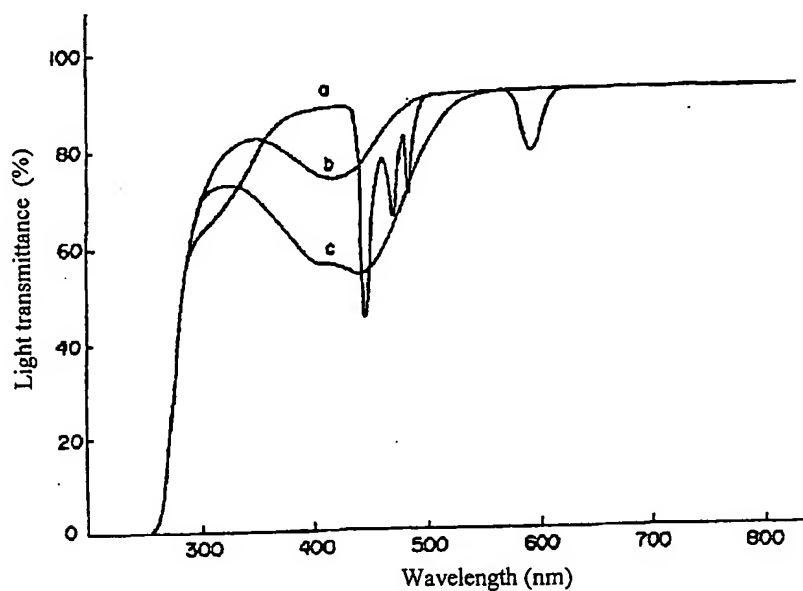


FIG. 1

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